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(54) METHOD FOR PRODUCING FINE PARTICLE OF POLYORGANOSILOXANE AND
LIQUID CRYSTAL DISPLAY DEVICE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for extremely effectively producing a fine particle of polyorganosiloxane capable of uniformly retaining the distance between the electrodes of a liquid crystal cell and the cell gap or the thickness of the liquid crystal layer formed between the electrodes of the liquid crystal cell when the fine particle is used in the internal portion of the layer between the electrodes of the liquid crystal cell and/or as a spacer for seal.

SOLUTION: An organosilicic compound shown by the formula $R_1aSi(OR_2)_{4-a}$ (R_1 is a 1-10C organic group selected from a substituted or nonsubstituted hydrocarbon group; R_2 is H or a 1-10C organic group selected from an alkyl group, an alkoxyalkyl group and an acyl group and n is an integer from 0 to 3) is added to a seed particle dispersing liquid containing a seed particle having hydrophobic surface and a surfactant, and the organosilicic compound is hydrolyzed in the presence of an alkaline to develop a seed particle.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention] This invention relates to the liquid crystal display using the polyorganosiloxane particle and this polyorganosiloxane particle which are obtained by the manufacture approach of a polyorganosiloxane particle, and this manufacture approach as a spacer. It is related with the still more detailed manufacture approach of the polyorganosiloxane particle to which this invention can manufacture the small polyorganosiloxane particle of particle diameter coefficient of variation by the short time and high yield. Moreover, this invention relates to the liquid crystal display using the polyorganosiloxane particle obtained by such approach as the spacer within a field, and a spacer for seals.

[0002]

[Background of the Invention] The liquid crystal display is formed from the liquid crystal layer with which the spacer within a field was interposed in inter-electrode [of the pair with which the liquid crystal cell for liquid crystal displays and this cel were equipped], and the liquid crystal matter was enclosed. By the way, if the thickness of this liquid crystal layer is not uniform, the fall of an irregular color or the contrast at the time of lighting may be caused in the image displayed on the liquid crystal cell. Moreover, when changing a display image at high speed, or when displaying an image with a large angle of visibility, it is required that the thickness of the liquid crystal layer inside a liquid crystal cell should be uniform. For this reason, the spacer within a field is expected for magnitude to be uniform.

[0003] Moreover, also about the seal section located in the periphery section of a liquid crystal layer, if thickness is not uniform, inter-electrode distance becomes less uniform, originates in this, and may cause problems, such as an irregular color of the same image, and a contrast fall at the time of lighting. For this reason, what has magnitude uniform also as a spacer for seals is used. Since organic system resin is used as a sealing compound, it is required for the seal section for which such a spacer for seals is used that the spacer for seals should have the good dispersibility to resin.

[0004] In recent years, it is required especially that thickness of the liquid crystal layer inside a liquid crystal cell should be further made into homogeneity with such a big screen liquid crystal display by using the big screen liquid crystal display in STN mode in order to display a big screen without an irregular color. Moreover, it is required that inter-electrode distance should be kept constant, keeping the area of the seal section small as much as possible, even if it is a big screen.

[0005] As such a spacer within a field, and a spacer for seals, conventionally, organic resin particles, such as polystyrene, the silica particle, or the organic resin covering silica particle was spherical, and the particle to which particle size was equal was used. However, when organic resin particles, such as polystyrene, were used as a spacer within a field of a liquid crystal cell, since it was too soft, the organic resin particle had the trouble that it was difficult to hold the thickness of the liquid crystal layer inside a liquid crystal cell to homogeneity. When the load of the uneven pressure was carried out to the liquid crystal layer inside a liquid crystal cell, the spacer within a field might deform according to dispersion in this pressure, and, specifically, the thickness of an internal liquid crystal layer might become an

ununiformity. Furthermore, organic resin particles, such as polystyrene, were too soft, and since deformation of a particle was large, there was also a problem that it was difficult to make inter-electrode distance into desired thickness in using it as a spacer for seals.

[0006] Moreover, when a silica particle was used as a spacer within a field of a liquid crystal cell and the particle size distribution of a silica particle were not sharp, the compression set of a silica particle originated in the small thing, and there was a trouble that the thickness of the liquid crystal layer inside a liquid crystal cell became an ununiformity. Furthermore, since the coefficient of thermal expansion of a liquid crystal layer differed from the coefficient of thermal expansion of a spacer inside a liquid crystal cell when the liquid crystal display using the silica particle as a spacer is put to low temperature, the trouble which an opening produces that the so-called low-temperature air bubbles were generated was also between the electrode of a liquid crystal cell, and the liquid crystal layer.

[0007] Since this silica particle was too hard, when it used as a spacer for seals, the electrode might be damaged and, occasionally the electrode might be disconnected further again. In order to solve the above troubles, after hydrolyzing the silicon compound which can be hydrolyzed, for example, a tetraethoxy silane etc., and preparing a silica particle, by JP,6-250193,A, using the silica particle which esterified the silanol group of this silica particle front face with the organic compound, and was obtained as an inter-electrode spacer of a liquid crystal cell is proposed.

[0008] Although the silica particle manufactured by this approach had moderate hardness and moderate mechanical stability, it was not what is not necessarily satisfied as an inter-electrode spacer of a liquid crystal cell. Moreover, in JP,7-140472,A, it is $R'_mSi(OR_2)_{4-m}$. (expressing R' in a formula, and the organic radical of specification $[R_2]$ respectively, m is the integer of 0-3.) It is indicated by heat-treating the organic silicon compound expressed by hydrolysis, and heat-treating the particle obtained by carrying out condensation polymerization at the temperature of 100-1000 degrees C that the spacer particle for liquid crystal cells which has specific compressibility is obtained. The compressibility of this spacer particle is controlled by residual organic radical weight after pyrolyzing a part of organic radical which exists in the interior of a particle by the above-mentioned heat treatment process. However, since the organic radical weight which remains inside a particle after the above-mentioned heat treatment process differed by this spacer particle when particle diameter differed, there was a trouble that control of the compressibility by residual organic radical weight was difficult, and it was difficult to adjust the compressibility of the spacer particle for liquid crystal cells to a desired value with the organic radical weight which for this reason the compression deformation for every particle does not become the same, therefore remains inside a particle. Moreover, over the particle whole from the outside of a particle differing in residual organic radical weight from the inside, compressibility had further the trouble that the compressive strength of the spacer particle for liquid crystal cells which the void occurred in a part for the organic base inside the particle by which the pyrolysis was carried out by the above-mentioned heat treatment process, consequently was obtained fell rather than was uniform.

[0009] Moreover, when this invention persons manufacture a polyorganosiloxane particle by the specific approach in JP,9-59384,A using a specific organic silicon compound, the particle which does not pass through the above heat treatment processes and to which the organic radical weight inside a polyorganosiloxane particle is controlled but, it has the high elastic recovery, and particle size was equal was obtained, and this particle has proposed that it is suitable as an inter-electrode spacer of a liquid crystal cell.

[0010] By the way, a particle suitable as a spacer, especially the particle with a small particle diameter coefficient of variation prepare a mono dispersion nuclear particle first, they repeat particle growth and the classification of this mono dispersion nucleus particle, perform and carry out particle growth, and are prepared. Since it was necessary by this preparation approach to make the addition rate of an organic silicon compound late when manufacturing a spacer particle, especially when big particle about 5 micrometers or more was obtained, there was a problem of requiring long duration extremely. Moreover, in order that gel detailed [in order to obtain the elastic particle which has suitable elasticity] when a specific organic silicon compound is used might carry out a byproduction, yield was low and it was difficult to obtain the particle to which magnitude was extremely equal.

[0011] Then, under such a situation, as a result of inquiring wholeheartedly that the above-mentioned trouble should be solved, when growing up the seed particle using the seed particle dispersion liquid containing a hydrophobic seed particle and a hydrophobic surfactant, this invention persons find out canceling each above-mentioned trouble, and came to complete this invention.

[0012]

[Objects of the Invention] When it uses as a spacer for seals, this invention It is rare for it to be also rare to distort an electrode, in order to distribute to the resin for seals at homogeneity and to carry out field contact with an electrode, therefore to damage an electrode. When inter-electrode distance can be kept highly precise to homogeneity and it uses as a spacer within a field The thickness of the liquid crystal layer inside a liquid crystal cell can be maintained to homogeneity with high precision, without damaging a protective coat, in order to carry out field contact with a protective coat. How to manufacture very efficiently the polyorganosiloxane particle which can be obtained by the liquid crystal display which does not have the problem which low-temperature air bubbles generate, either, and was excellent in the display engine performance for this reason, and this polyorganosiloxane particle, And it aims at offering the liquid crystal display which made this polyorganosiloxane particle placed between inter-electrode [of a liquid crystal cell] as the spacer for seals, and a spacer within a field.

[0013]

[Summary of the Invention] The manufacture approach of the polyorganosiloxane particle concerning this invention is characterized by adding the organic silicon compound expressed with the following type (1), hydrolyzing this organic silicon compound under existence of alkali, and growing up a seed particle into the seed particle dispersion liquid containing the seed particle who has a hydrophobic front face, and a surfactant.

[0014]

$R_1nSi(OR_2)_{4-n}$ (1)

(R₁ is the organic radical of the carbon numbers 1-10 chosen from a permutation or an unsubstituted hydrocarbon group among a formula. R₂) it is the organic radical of the carbon numbers 1-10 chosen from a hydrogen atom or an alkyl group, an alkoxyalkyl group, and an acyl group, and n is the integer of 0-3. Said seed particle may carry out hydrophobing of the front face of a hydrophilic seed particle. Further again a seed particle While the water layer as the organic silicon compound layer and lower layer as the upper layer **** the organic silicon compound expressed with the following type (1), and water to extent which is not mixed completely, an organic solvent, alkali, and a surfactant are added to a water layer. All over a water layer You may be hydrolysis and the silica system seed particle obtained by carrying out condensation polymerization about an organic silicon compound under existence of a surfactant.

[0015]

$R_1nSi(OR_2)_{4-n}$ (2)

(R₁ is the organic radical of the carbon numbers 1-10 chosen from a permutation or an unsubstituted hydrocarbon group among a formula. R₂) it is the organic radical of the carbon numbers 1-10 chosen from a hydrogen atom or an alkyl group, an alkoxyalkyl group, and an acyl group, and n is the integer of 1-3. By the manufacture approach of the polyorganosiloxane concerning this invention After growing up a seed particle, a polyorganosiloxane particle is separated from the obtained polyorganosiloxane particle dispersion liquid. It is desirable to dry and/or heat-treat this polyorganosiloxane particle under air or an inert gas ambient atmosphere in a 100-1200-degree C temperature requirement.

[0016] The polyorganosiloxane particle concerning this invention is obtained by said approach, and is in the range whose mean particle diameter is 1-30 micrometers, and compressibility is in the range of 2 200 to 6000 Kgf/mm 10%, and it is characterized by a CV value being 10% or less. The liquid crystal display concerning this invention is characterized by said polyorganosiloxane particle having the liquid crystal cell used as a spacer.

[0017]

[Detailed Description of the Invention] The manufacture approach of the polyorganosiloxane particle concerning the manufacture approach **** of a polyorganosiloxane particle and this invention is

explained concretely.

[preparation of seed particle dispersion liquid] -- by this invention, the seed particle dispersion liquid containing a seed particle and a surfactant are prepared first.

[0018] As a seed particle, if it is particles, such as an inorganic oxide, an organic inorganic composite particle, and an organic high-molecular-compound particle, it can be especially used without a limit. As an inorganic oxide particle, an oxide particle with conventionally well-known a silica, an alumina, a zirconia, a titania, silica alumina, a silica zirconia, etc. and a multiple oxide particle are mentioned. The organic inorganic composite particle obtained by hydrolyzing a metal alkoxide and/or a metal alkyl alkoxide as an organic inorganic composite particle is mentioned. Furthermore, as an organic high molecular compound particle, resin particles, such as a divinylbenzene polymer, a divinylbenzene-styrene copolymer, and a divinylbenzene-acrylic ester copolymer, a phenol resin particle, etc. are mentioned.

[0019] In this invention, the seed particle which has a hydrophobic front face is used. For this reason, as for the hydrophilic seed particle which has the OH radical of a hydrophilic property on a front face, it is desirable that process by surface treatment agents, such as a silane coupling agent and a titanium coupling agent, and the hydrophobic functional group is introduced into the front face like [that what has a hydrophobic front face like an organic high-molecular-compound particle can be used as it is] an oxide particle and a multiple oxide particle. In addition, after introducing a hydroxyl group by making an alkaline solution contact when inadequate even if it does not have the hydroxyl group on a seed particle front face or being had (this may be called activation process of a seed particle), it may process by a silane coupling agent etc. similarly, and a hydrophobic functional group may be given to a front face.

[0020] Thus, the seed particle which has hydrophobicity has high compatibility with a surfactant, and since it will be in the condition that the surfactant met on the seed particle front face, the hydrolyzate (hydrolyzate which the hydrophobic organic radical coupled directly with the silicon atom) of an organic silicon compound is incorporated by this at a surfactant layer and it deposits on a seed particle front face further with the compatibility of the hydrophobic functional group of a seed particle front face, and the hydrophobic organic radical of a surfactant, particle growth can be performed efficiently.

[0021] As for the mean particle diameter of a seed particle, it is desirable that it is in the range of 0.05-10.0 micrometers, and it is desirable that it is in the range which is 0.5-7.0 micrometers especially. As for the particle diameter coefficient of variation of such a seed particle, it is desirable that it is 20% or less. When 20% was exceeded, and the particle diameter coefficient of variation of the polyorganosiloxane particle finally obtained becomes large and it uses as a spacer, there is a problem of inter-electrode distance not being made to regularity.

[0022] Moreover, both an ionic surfactant and a nonionic surfactant can be used as a surfactant used at the time of seed particle dispersion-liquid preparation. As such a surfactant, if meltable in water, it is possible to use it without a limit especially. Specifically Cationic surfactants, such as an alkylamine salt and quarternary ammonium salt, Amphoteric surface active agents, such as an alkyl betaine and amine oxide, a fatty-acid salt, Alkyl-sulfuric-acid ester, alkyl naphthalenesulfonate, alkyl sulfo succinate, Alkyl diphenyl ether disulfon acid chloride, alkyl next door acid chloride, polyoxyethylene alkyl-sulfuric-acid ester, Anionic detergents, such as a polyoxyethylene alkyl allyl compound sulfate and a naphthalene sulfonic-acid formalin condensate, Polyoxyethylene alkyl ether, polyoxyethylene alkyl aryl ether, A polyoxyethylene derivative, a sorbitan fatty acid ester, a polyoxy ECHIRE sorbitan fatty acid ester, Nonionic surfactants, such as polyoxyethylene sorbitol fatty acid ester, a glycerine fatty acid ester, polyoxyethylene fatty acid ester, polyoxyethylene alkylamine, and an alkyl alkanol amide, etc. are mentioned. In addition, if caustic alkali of sodium, ammonia, etc. are added as for example, a hydrolysis catalyst and the dispersion medium used presents alkalinity, an anionic surfactant will be used suitably.

[0023] As for the addition of this surfactant, it is desirable that it is in 0.4 - 40% of the weight of the range to a hydrophobic seed particle. If the surfactant is contained in the above-mentioned range, as for a deposit and the organic silicon compound which carries out condensation polymerization and which is contributed to particle growth, comparatively (utilization factor of an organic silicon compound) will

become [the hydrolyzate of the organic silicon compound added in order to grow up a seed particle] high on a hydrophobic seed particle front face. It decreases that new karyogenesis is controlled and many gel objects remain, for this reason, the yield of a particle improves, and since particle growth becomes uniform, a particle with a low particle diameter coefficient of variation can obtain.

[0024] As a dispersion medium which distributes a hydrophobic seed particle, the mixed solvent of water and/or an organic solvent is used. As an organic solvent, one sort chosen from water and the organic solvent of compatibility, for example, alcohols, glycols, glycol ether, and ketones or two sorts or more are used. In addition, as for the concentration of the organic solvent in a mixed solvent, it is desirable that it is 30% or less.

[0025] In addition, although the concentration of the hydrophobic seed particle in dispersion liquid is based also on particle diameter, it is desirable that it is in 0.05 - 10% of the weight of the range. It is in the inclination which the particle which will be obtained if productivity is low and exceeds 10 % of the weight condenses at less than 0.05 % of the weight. The dispersion liquid of a seed particle may irradiate a supersonic wave if needed, and may carry out mono dispersion of the particle.

[0026] After it may be beforehand added by the dispersion medium and a surfactant makes a dispersion medium distribute a seed particle, it may be added by dispersion liquid. Moreover, as seed particle dispersion liquid, it is the following and the silica system seed particle dispersion liquid made and prepared can also be used.

In preparation this invention of silica system seed particle dispersion liquid First, while the water layer as the organic silicon compound layer and lower layer as the upper layer agitates the organic silicon compound (it is henceforth called an organic silicon compound (A)) expressed with the following type (1), and water to extent which is not mixed completely An organic solvent, alkali, and a surfactant are added to a water layer, all over a water layer, it hydrolyzes, condensation polymerization of the organic silicon compound (A) is carried out to the bottom of existence of a surfactant, and the dispersion liquid of a silica system seed particle are prepared.

[0027]

$R_1nSi(OR_2)_{4-n}$ -- (1) (the inside of a formula and n are the integers of 1-3)

R₁ expresses the organic radical of the carbon numbers 1-10 chosen from a permutation or an unsubstituted hydrocarbon group among the above-mentioned formula. As an unsubstituted hydrocarbon, an alkyl group (a chain-like alkyl group or annular alkyl group), an alkenyl radical, an aralkyl radical, an aryl group, etc. are mentioned. Among these, as a permutation hydrocarbon By the radical permuted by atoms other than a non-hydrocarbon group or hydrogen, a part or all of a hydrogen atom of a hydrocarbon Specifically, a chloro alkyl group, gamma-methacryloxypropyl radical, gamma-glycidoxy propyl group, an aminopropyl radical, 3, 4-epoxycyclohexyl ethyl group, gamma-mercapto propyl group, a trifluoro propyl group, a fluorocarbon radical, etc. are mentioned.

[0028] R₂ is the organic radical of the carbon numbers 1-10 chosen from a hydrogen atom or an alkyl group, an alkoxyalkyl group, and an acyl group. As such an organic silicon compound (A), concretely Methyl trimetoxysilane, Methyl triethoxysilane, a methyl triisopropoxy silane, a methyl tris (methoxyethoxy) silane, Ethyltrimethoxysilane, vinyltrimetoxysilane, phenyltrimethoxysilane, Gamma-chloropropyltrimetoxysilane, gamma-glycidoxypropyltrimetoxysilane, The organic silicon compound under [n= 1] above (1) of methyltriacetoxysilane, phenyl triacetoxysilane, etc., Dimethoxy dimethylsilane, diethoxy-3-glycidoxypropylmethylsilane, The organic silicon compound under [n= 2] above (1) of a dimethoxy diphenyl silane, diacetoxymethylsilane, diphenyl silane diol, etc., The organic silicon compound in [n= 3] the above-mentioned formulas (1), such as trimethylmethoxysilane, trimethylethoxysilane, acetoxymethylsilane, and a trimethyl silanol, is mentioned. In addition, compared with the organic silicon compound of 2 or 3, the hydrolysis rate of n is [the organic silicon compound of n= 1] early.

[0029] Although these organic silicon compounds (A) can also be used independently, they can also mix and use two or more sorts. When using the organic silicon compound (A) independently expressed with a formula (1), the organic silicon compound (A) of n= 1 is desirable. Moreover, when mixing and using two or more sorts of organic silicon compounds (A) with which n differs, it is desirable that 50% or

more of the organic silicon compound (A) to be used is an organic silicon compound (A) of $n=1$. When the organic silicon compound (A) of $n=1$ uses it at less than 50%, the yield of the seed particle obtained may fall, and it may become the inclination for a CV value to become high.

[0030] The amount of the water used at the process (a) of this invention should just be more than a complement at hydrolysis of an organic silicon compound (A). Specifically what is necessary is just more than the number of mols of OR2 radical weight in the organic silicon compound (A) to be used, and equivalence. Moreover, although especially the upper limit of the amount of water is not limited, it is especially desirable that it is less than [of OR2 radical weight in an organic silicon compound (A) / 50 mol twice]. Since the hydrolyzate concentration in the inside of a water layer is too low when the amount of water exceeds the 50-mol twice of OR2 radical weight, the thing of a desired particle size may not be obtained.

[0031] In addition, the organic silicon compound (A) expressed with the formula (1) used by this invention is hydrophobicity, and since a hydrolysis rate is also slow, it does not mix with water but it forms vertical two-layer one. Usually, since specific gravity is lighter than water, a lower layer is a water layer and, as for an organic silicon compound (A), the upper layer turns into an organic silicon compound (A) layer. While two-layer agitates to extent which is not mixed completely in this condition, an organic solvent, alkali, and a surfactant are added to a water layer. Furthermore, water may be added if needed.

[0032] Although churning changes also with the dissolution rate to the mixed solvent of the water of the upper organic silicon compound (A), and an organic solvent, and reactivity, it is desirable to agitate in the condition that an organic silicon compound (A) layer and a water layer do not mix or suspend completely, and it is desirable that it is extent which the organic solvent in which especially an organic silicon compound (A) layer and a water layer carry out two-layer separation, and which they add to a water layer, alkali, and a surfactant can mix to homogeneity promptly.

[0033] By addition of an organic solvent, water becomes a mixed solvent with an organic solvent, and an organic silicon compound (A) dissolves into this mixed solvent. With the added alkali, it hydrolyzes, condensation polymerization of the organic silicon compound (A) which dissolved into the mixed solvent is carried out, and a silica system seed particle is obtained. Since this silica system seed particle has the hydrocarbon R1 originating in an organic silicon compound (A), it shows hydrophobicity.

[0034] There are water and compatibility, and as an organic solvent, especially if it is the organic solvent which can dissolve an organic silicon compound (A), it is not restricted, and one sort chosen from alcohols, glycols, glycol ether, and ketones or two sorts or more are used. As for the total quantity of such water and the organic solvent to add, it is desirable that the seed particle concentration in the silica system seed particle dispersion liquid finally obtained is the amount which becomes about 0.05 - 10 % of the weight by SiO₂ conversion.

[0035] Moreover, as alkali added, an alkali-metal water solution, a quarternary-ammonium-salt water solution, amines, an aqueous ammonia solution, ammonia gas, etc. are mentioned. Among these, it *****s easily by desiccation and heat-treatment, and since it does not remain in the polyorganosiloxane particle moreover obtained, especially an aqueous ammonia solution and ammonia gas are used preferably. In addition, such alkali functions as a hydrolysis catalyst of an organic silicon compound (A).

[0036] Although not restricted especially as an addition of such alkali, it is desirable 7-13, and that extent which can maintain the mixed solvent of water and an organic solvent to alkalinity, i.e., pH of a mixed solvent, is added so that it can maintain in the range of 8-12 preferably. If alkali is added maintaining pH of such range, the reaction rate of an organic silicon compound (A) will become quick, and a seed particle [mono dispersion moreover] will be obtained.

[0037] In this invention, a surfactant is added with such an organic solvent and alkali. The above mentioned thing and the same thing are illustrated as a surfactant. As for the addition of a surfactant, it is desirable that it is in 0.1 - 5% of the weight of the range of an organic silicon compound (A).

[0038] By this approach, the small seed particle of particle diameter rate of change can be obtained by high yield, without a gel object remaining by adding a surfactant at the time of seed particle preparation.

Although this reason is not clear, in the front face of the gel very fine particle which the end of hydrolyzate and a condensation polymer or condensation polymer of an organic silicon compound (A) condensed and generated. The hydrophobic organic radical combined with the direct silicon atom exists. With the compatibility of this organic radical and the hydrophobic organic radical of a surfactant it is thought that a particle (micell Mr. particle) like the micell which has the magnitude of about 1 law to which the hydrophobic organic radical and the surfactant met is formed, and this micell Mr. particle gathers and joins together, and forms the seed particle of uniform particle diameter. for this reason, since there is too much surfactant when the amount of a surfactant does not form the micell Mr. particle which has large **** of about 1 law described above since less than 0.1% of the weight of a case had little surfactant but exceeds 5 % of the weight, micell Mr. particles cannot gather, the seed particle of uniform particle diameter cannot be formed, but it is thought that the condition of a micell Mr. particle is maintained.

[0039] even if it adds these organic solvents, a surfactant, and alkali according to an individual in a water layer -- giving up -- ** -- moreover, an organic solvent and a surfactant may be mixed beforehand and you may add. Moreover, the whole quantity may be added collectively, and you may add intermittently in several steps, and these addition may be added still more nearly continuously. It is desirable to add so that it may become comparable as the rate at which an organic silicon compound (A) hydrolyzes and these addition rates disappear especially.

[0040] At the above seed particle preparation processes, hydrolysis and a condensation polymerization reaction are [about]. -It is desirable to carry out in a 5-20-degree C temperature requirement. Moreover, as for the mean particle diameter of the seed particle obtained, it is desirable that it is in the range of 0.05-10.0 micrometers, and it is desirable that it is in the range which is 0.5-7.0 micrometers especially. In this way, the obtained silica system seed particle dispersion liquid may adjust seed particle concentration and surfactant concentration if needed.

[0041] [Seed particle growth process] Subsequently, dissolve one sort or two sorts or more of mixture (it is henceforth called an organic silicon compound (B)) of an organic silicon compound shown by the following formula (2) in an organic solvent if needed, add to the above seed particle dispersion liquid, add alkali as a hydrolysis catalyst further, make an organic silicon compound hydrolyze, a seed particle front face is made to carry out hydrolyzate a deposit and condensation polymerization, and a seed particle is grown up.

[0042]



R₁ is the organic radical of the carbon numbers 1-10 chosen from a permutation or an unsubstituted hydrocarbon group among a formula, R₂ is the organic radical of the carbon numbers 1-10 chosen from a hydrogen atom or an alkyl group, an alkoxyalkyl group, and an acyl group, and n is the integer of 0-3.

[0043] As an organic silicon compound whose n in a formula (2) is 0, a tetramethoxy silane, a tetraethoxy silane, tetra-propoxysilane, tetramethyl methoxysilane, a tetraethyl ethoxy silane, tetraacetoxysilane, etc. are mentioned. Moreover, as a compound of 1-3, said illustrated thing and the same thing are mentioned for n.

[0044] In addition, when using the silica system seed particle dispersion liquid prepared as seed particle dispersion liquid using the above mentioned organic silicon compound (A), an organic silicon compound (B) may be the same as the organic silicon compound (A) used at the time of silica system seed particle dispersion-liquid preparation, or may differ. Although these organic silicon compounds (B) can also be used independently, they can also mix and use two or more sorts. When using it independently, the thing of 1 has desirable n by the above-mentioned formula (2), and when using two or more sorts for the organic silicon compound (B) with which the values of n differ, mixing, it is desirable that 50% or more of an organic silicon compound (B) is [n] an organic silicon compound (B) of 1. n of n is more desirable than the organic silicon compound (B) of 2 or 3 at the point that a hydrolysis rate is early, and since yield tends to fall when n is [the organic silicon compound (B) of 1] less than 50%, the organic silicon compound (B) of 1 is not desirable.

[0045] The addition of an organic silicon compound (B) should just add a complement to obtain the

polyorganosiloxane particle of desired particle diameter. Although the addition rate of the organic silicon compound at this time (B) is suitably chosen by the class of the concentration of the seed particle in seed particle dispersion liquid, particle diameter, or organic silicon compound (B) etc., it is desirable to add an organic silicon compound (B) so that an average particle growth rate may become an hour in 0.01-5micrometers /. When an average particle growth rate exceeds an hour in 5micrometers /, the addition rate of an organic silicon compound (B) is too quick, and a detailed particle does not carry out a byproduction, or by a particle not growing up to be homogeneity, when an average particle growth rate is less than 0.01micrometers/hour, the homogeneity of particle diameter does not improve further.

[0046] As alkali added as a catalyst for hydrolysis, although an alkali-metal hydroxide water solution, an amine water solution, an aqueous ammonia solution, ammonia gas, etc. are mentioned, ammonia cannot remain easily after heat-treatment and in a particle, and since an aqueous ammonia solution and ammonia gas are moreover cheap, they are desirable. Although the addition of alkali changes with the classes and amounts of the organic silicon compound (B) to be used, pH of dispersion liquid is desirable and it is desirable 7-13, and to add continuously or intermittently so that it may become the range of 8-12 still more preferably.

[0047] Moreover, water and/or an organic solvent which was described above can be added if needed. It may maintain to the temperature at the time of organic silicon compound hydrolysis and hydrolysis, this **, or an elevated temperature, and you may ripe a polyorganosiloxane particle. According to this aging process, the particle diameter of the particle obtained serves as homogeneity further. As for the temperature and time amount at the time of aging, it is preferably desirable to maintain at the temperature of 50-90 degrees C for about 0.5 to 24 hours about 20-95 degrees C. A hydrolysis rate is slow, it is hard to obtain the particle which the silica component which remains dissolving since hydrolyzate does not deposit enough depending on the organic silicon compound which maturing temperature uses at less than about 20 degrees C increased, and carried out mono dispersion, condensation of particles takes place above 95 degrees C, and the particle welded further may generate.

[0048] If it manufactures by such approach, the utilization ratio of an organic silicon compound expressed with the formula (2) used at the time of seed particle growth can be made high, and the polyorganosiloxane particle which has desired particle diameter, particle diameter coefficient of variation, and elasticity for this reason can be manufactured efficiently.

A polyorganosiloxane particle is separated from the polyorganosiloxane particle dispersion liquid obtained at the [separation and desiccation / heating down-stream-processing] above-mentioned process.

[0049] As the separation approach of a polyorganosiloxane particle, well-known approaches, such as filtration and centrifugal separation, are conventionally employable. An organic solvent may wash the separated polyorganosiloxane particle. The separated polyorganosiloxane particle responds to the application (the spacer within a field, spacer for seals) used, and is dried and/or heat-treated under air or an inert gas ambient atmosphere in a 100-1200-degree C temperature requirement. In addition, even if whenever [stoving temperature] heat-treats at the temperature which less than 100 degrees C of hardness, compressibility, etc. of a polyorganosiloxane particle are insufficient, and exceeds 1200 degrees C, the hardness and compressibility of a polyorganosiloxane particle do not become high further.

[0050] For example, if it heat-treats at the temperature of 600 degrees C or more among air, a polyorganosiloxane particle suitable as a spacer for seals will be obtained. Moreover, if it heat-treats at the temperature of about 100-600 degrees C, a polyorganosiloxane particle suitable as a spacer within a field will be obtained. Under the inert gas ambient atmosphere, if a polyorganosiloxane particle is heat-treated at the temperature of 400-600 degrees C or more, a black polyorganosiloxane particle is obtained and it excels in display engine performance -- contrast of the liquid crystal display [using this particle as a spacer within a field] improves -- further again.

[0051] According to the manufacture approach of the polyorganosiloxane particle concerning above this inventions, since an organic silicon compound is added and a hydrophobic seed particle is made to carry out particle growth under existence of a surfactant, there is also no byproduction of detailed gel, and

while being able to obtain the big particle which has uniform particle diameter for a short time, the polyorganosiloxane particle made into the purpose can be obtained with sufficient repeatability by high yield.

[0052] A polyorganosiloxane particle, next the polyorganosiloxane particle concerning this invention are explained concretely. The polyorganosiloxane particle concerning this invention is obtained by the above-mentioned approach, and 1-30 micrometers of mean particle diameter are in the range of 2-20 micrometers preferably.

[0053] Although the mean particle diameter of a polyorganosiloxane particle can be set up in consideration of elasticity with the class of liquid crystal display, and the thickness of a liquid crystal layer to need, what separates from the above-mentioned range is not usually used as a spacer. Moreover, a polyorganosiloxane particle has still more preferably 0.5 - 10% of coefficient-of-variation CV values of particle diameter in 0.5 - 3% of range preferably 10% or less. When the coefficient of variation of particle diameter is high exceeding 10%, inter-electrode thickness cannot be held to homogeneity, but image nonuniformity etc. may be started or an electrode may be damaged.

[0054] In addition, the mean particle diameter and coefficient of variation of the polyorganosiloxane particle concerning this invention and said seed particle photo a particle using a scanning electron microscope (JEOL [Co., Ltd.] make: JSM-5300 mold), and are measured using image-analysis equipment (Asahi Chemical [Co., Ltd.] make: IP-1000) about 250 particles of this image. The coefficient-of-variation CV value of particle diameter asks for the standard deviation of each particle diameter of 250 particles, mean particle diameter, and particle diameter, and is acquired from the following formula by count.

[0055] $\text{valve flow coefficient} = (\text{particle diameter standard deviation (sigma)} / \text{mean particle diameter (Dn)}) \times 100$ [0056]

[Equation 1]

$$\text{粒子径標準偏差} (\sigma) = \sqrt{\sum_{i=1}^n |D_i - D_n|^2 / (n-1) \times D_n}$$

D_i : 個々の粒子の粒子径、 n : 250

[0057] Moreover, 10% compressibility of the polyorganosiloxane particle concerning this invention is in the range of 2 200 to 6000 Kgf/mm. When using the polyorganosiloxane particle concerning this invention as a spacer within a field of a liquid crystal display, what has compressibility in the range of 2 200 to 1000 Kgf/mm 10% is used.

[0058] 10%, when using a polyorganosiloxane particle as a spacer within a field, since the particle is soft, the deformation of a spacer of compressibility is large and it may be unable to hold thickness of the liquid crystal layer inside a liquid crystal cell to homogeneity less than [200 Kgf(s)/mm] by two. Moreover, when the pressure concerning each spacer tends to be reduced and it is going to control deformation, the spraying number of a polyorganosiloxane particle must be made to increase and problems, such as a fall of the quality of the liquid crystal display accompanying this and economical efficiency, may arise. In addition, there is a problem of low-temperature gassing which compressibility described above exceeding 2 1000 Kgf(s)/mm 10% when high.

[0059] Moreover, when using the polyorganosiloxane particle concerning this invention as a spacer for the seal sections, what has compressibility in the range of 2 about 1000 to 6000 Kgf/mm 10% is used. In order to reduce the pressure which spends 10% for compressibility to each spacer less than [about 1000 Kgf(s)/mm] by two and to control deformation, the spraying number increases, and it becomes easy to change inter-electrode distance, and image nonuniformity may be started. Moreover, 6000 Kgf(s)/mm, exceeding 2, compressibility may damage the glue line on an electrode substrate and an electrode substrate, a coat layer, etc. 10%, when high.

[0060] In addition, the evaluation approach of such 10% compressibility is as follows. the particle whose 10% compressibility is one piece whose particle size is D as a sample, using a minute compression tester (Shimadzu make MCTM-200) as a measuring instrument -- using -- a load rate fixed in a sample -- a load -- a load -- carrying out -- compression -- a particle is transformed until a variation

rate becomes 10% of particle diameter -- making -- 10% -- a variation rate -- the load at the time, and compression -- it asks for a variation rate (mm). the particle size and the compressive load, and compression for which it asked -- it asks by calculating a variation rate by substituting it for a degree type.

[0061]

$E = (3/21/2)$ and $F - (1 - K^2) - S - 3/2$ and $D - 1/2$ -- here E: -- compressibility (Kgf/mm²)

F: Compressive load (kg)

K: The Poisson's ratio of a particle (a constant, 0.38)

S: Compression displacement (mm)

D: It is particle diameter (mm).

[0062] On these specifications, about ten particles, compressibility was evaluated 10% separately and these averages were made into 10% compressibility of a particle.

A liquid crystal display, next the liquid crystal display concerning this invention are explained concretely. The liquid crystal display concerning this invention has the liquid crystal cell equipped with the electrode of a pair, and the above-mentioned polyorganosiloxane particle is used for inter-electrode [said] as a spacer (inter-electrode spacer).

[0063] The above-mentioned liquid crystal display is constituted like the well-known liquid crystal display except for the inter-electrode distance of a liquid crystal cell being uniformly held as a spacer using the polyorganosiloxane particle concerning this invention. In the liquid crystal display concerning this invention, the polyorganosiloxane particle may intervene over the whole electrode surface surface of a liquid crystal cell (spacer within a field), and may intervene in the adhesives layer of the inter-electrode periphery section (seal section) (spacer for seals).

[0064] When using the polyorganosiloxane particle concerning this invention as a spacer within a field of a liquid crystal cell, as for a polyorganosiloxane particle, 2 and the thing 200 to 7000 Kgf/whose mm is in the range of the range of 2 preferably are suitably used for compressibility 200 - 1000 Kgf/mm abbreviation 10%. If compressibility is in the aforementioned range 10%, while there will be little spraying number and it will end, damage and the low-temperature air bubbles of an electrode surface or a protective coat can be reduced.

[0065] Moreover, when using a polyorganosiloxane particle as a spacer for seals, that to which a polyorganosiloxane particle has compressibility in the range of 2 about 1000 to 6000 Kgf/mm 10% is used suitably. Image nonuniformity may be started, when compressibility needs to make [many] the spraying number less than [about 1000 Kgf(s)/mm] by two 10%, and it becomes easy to change inter-electrode distance and inter-electrode distance cannot be especially kept constant. 10%, 6000 Kgf (s)/mm, exceeding 2, compressibility may damage the glue line or coat layer on an electrode substrate and an electrode substrate, when high.

[0066] The particle size and the CV value of a polyorganosiloxane particle which are used are suitably chosen according to the magnitude of the inter-electrode distance needed and a cel gap, homogeneity, etc. As for the CV value of a polyorganosiloxane particle, it is especially preferably desirable that it is 5% or less of range 10% or less. When using a polyorganosiloxane particle as an inter-electrode spacer within a field of a liquid crystal cell, a liquid crystal cell is the following, and is made and manufactured.

[0067] A polyorganosiloxane particle is first sprinkled by well-known approaches, such as a wet method or dry process, to one electrode surface (when the protective coat is formed on the electrode surface, it is the front face of a protective coat). Although it is not limited, its approach of spraying using a nozzle etc. is common, and since especially the sewage sprinkling at this time can sprinkle a polyorganosiloxane particle to homogeneity, it is desirable. In addition, when the spraying consistency of a polyorganosiloxane particle is uneven, the thickness of the interior liquid crystal layer of a liquid crystal cell may ununiformity-ize, and the problem of image display nonuniformity and low-temperature air bubbles may arise by this.

[0068] Next, the electrode surface (or front face of a protective coat) of another side is laid on the polyorganosiloxane particle sprinkled by the electrode surface (or front face of a protective coat), and

superposition and a cel gap are formed. Then, it is filled up with a liquid crystal ingredient into the formed cel gap, and the liquid crystal cell used with the liquid crystal display applied to this invention lamination and by sealing by the resin for seals in the periphery section of a two-electrodes side is obtained. In this case, it is desirable to mix the polyorganosiloxane particle which starts this invention into the resin for seals.

[0069] Moreover, such a liquid crystal cell applies to the periphery section of one electrode surface (or front face of a protective coat) the resin for seals with which the polyorganosiloxane particle concerning this invention is mixed except for the inlet of a liquid crystal ingredient, and after it subsequently lays the electrode surface (or front face of a protective coat) of another side and pours in a liquid crystal ingredient from the inlet of superposition and a liquid crystal ingredient, it can obtain it also by the approach of sealing the inlet of this liquid crystal ingredient by the resin for seals.

[0070] The liquid crystal display concerning such this invention does not start image nonuniformity while the inter-electrode distance of a liquid crystal cell is held uniformly, there is little spraying number, and it ends and it can reduce damage and the low-temperature air bubbles of an electrode surface or a protective coat, since the specific polyorganosiloxane particle is used as a spacer.

[0071]

[Effect of the Invention] According to this invention, the method of manufacturing very efficiently the polyorganosiloxane particle to which it has desired elasticity and particle size was equal is offered. That is, in this invention, by adding an organic silicon compound and making a hydrophobic seed particle carry out particle growth under existence of a surfactant, there is also no byproduction of detailed gel and the big particle which has uniform particle diameter for a short time can be obtained. Moreover, according to such a manufacture approach, the polyorganosiloxane particle in which detailed gel does not carry out a byproduction but which it makes the purpose by high yield can be obtained with sufficient repeatability.

[0072] Moreover, its particle size distribution are sharp, and since the obtained polyorganosiloxane particle has compressibility in the range of 2 200 to 6000 Kg/mm 10%, it is suitable as the inter-electrode interior of a field and/or the inter-electrode spacer for seals. If the polyorganosiloxane particle concerning this invention is used as the inter-electrode interior of a field and/or the inter-electrode spacer for seals of a liquid crystal cell, since the particle size distribution of this particle are sharp By being able to hold to homogeneity the thickness of the inter-electrode distance of a liquid crystal cell, and a cel gap, i.e., the liquid crystal layer formed in inter-electrode [of a liquid crystal cell], and choosing the polyorganosiloxane particle of suitable compressibility There is little spraying number, and it ends, the low-temperature air bubbles generated inside a liquid crystal cell are prevented, and the liquid crystal display of the high performance whose contrast there is no image unevenness etc. and improved can be offered by choosing a still blacker polyorganosiloxane particle.

[0073]

[Example] Hereafter, although an example explains this invention, this invention is not limited to these examples.

[0074]

[Example 1] Solution temperature was adjusted at 0**1 degree C, having put in 13,162g of pure water and agitating in the container of preparation content volume 20L of seed particle dispersion liquid. Furthermore, methyl trimetoxysilane (methyl trimetoxysilane) 1,500g beforehand adjusted to the temperature of 5 degrees C was added calmly, and methyl trimetoxysilane and pure water considered as the condition of having separated into vertical two-layer one. Then, it cooled, agitating until the temperature of the upper methyl trimetoxysilane became 1**1 degree C.

[0075] Separately, 2.70g of aqueous ammonia of butyl alcohol 6.98g and 28% of concentration was added to 279.2g of pure water, 15.0g (octyl naphthalene sulfonic-acid sodium) of anion system surface active agents was added to this, and the surface-active-agent mixed solution which adjusted temperature to 5**1 degree C was prepared. It added over 60 minutes in the lower layer (water layer) which divided the obtained surfactant mixed solution into vertical two-layer ones, agitating to extent which the upper layer and a lower layer do not mix completely.

[0076] Churning was performed succeedingly for 2 hours and the dispersion liquid of a hydrophobic seed particle (S-1) were prepared. A part of these hydrophobic seed particle dispersion liquid were extracted, the hydrophobic seed particle was separated and washed, subsequently it dried at 110 degrees C for 2 hours, and the powder of a hydrophobic seed particle was obtained. Scanning electron microscope photograph observation of the obtained hydrophobic seed particle was performed, and the particle size distribution and the particle-size coefficient-of-variation CV value of a seed particle were evaluated. The result was shown in the table.

[0077] Maintaining solution temperature for the 14,965.5 g dispersion liquid of the hydrophobic seed particle which is the growth above of a seed particle, and was made and prepared at 0**1 degree C, methyl trimetoxysilane 6,008g, 23,527.7 g pure-water [which carried out the temperature control to 5**3 degrees C], and butyl alcohol 588.6g, and the mixed liquor of 4.8g of aqueous ammonia of 28% of concentration were added in 24 hours, respectively, the hydrophobic seed particle was grown up, and polyorganosiloxane particle dispersion liquid (PS-1) were prepared.

[0078] The polyorganosiloxane particle was separated and washed from the heat-treatment dispersion liquid of a polyorganosiloxane particle, and, subsequently it dried at 110 degrees C for 2 hours. Subsequently, under the nitrogen-gas-atmosphere mind containing 10% of ammonia gas, it heat-treated at 440 degrees C for 3 hours, and the polyorganosiloxane particle (P-1) was obtained. It asked for particle size distribution, a particle-size coefficient-of-variation CV value, and 10% compressibility about the obtained polyorganosiloxane particle.

[0079] A result is shown in Table 1. Moreover, the yield of the particle calculated from the amount of theoretical generation of the particle calculated from the amount of the methyl trimetoxysilane used and the weight of the actually obtained particle was 95.2%. With in addition, the amount of theoretical generation of the particle calculated from the amount of the methyl trimetoxysilane used It is the weight computed noting that used $R_1nSi(OR)_2(4-n)$ becomes polyorganosiloxane $(R_1nSiO(4-n)/2)$ by hydrolysis. Yield Weight (g) after heat-treating the particle actually obtained as shown in the following type at 440 degrees C for 3 hours is *(ed) by the weight computed noting that $R_1nSi(OR)_2(4-n)$ becomes polyorganosiloxane $(R_1nSiO(4-n)/2)$ by hydrolysis.

[0080]

[Equation 2]

$$\text{収率} = \frac{\text{実際に得られた粒子を 440℃で3時間加熱処理した後の重量}}{\text{有機ケイ素化合物から計算されるポリシロキサン理論重量}} \times 100$$

[0081]

[Example 2] The polyorganosiloxane particle (P-1) obtained in the example 1 was heat-treated at 1000 degrees C among air for 1 hour, and the polyorganosiloxane particle (P-2) was obtained. It asked for particle size distribution, a particle-size coefficient-of-variation CV value, and 10% compressibility about the obtained polyorganosiloxane particle (P-2).

[0082] A result is shown in Table 1.

[0083]

[Example 3] 2000g pure water was made to distribute this using 100g (the product made from Industry: catalyst formation 1.0% of SW mean-particle-diameter [of 5.0 micrometers] particle diameter coefficient of variation, 4800 kgf/mm 10% K value 2) of preparation silica particles of a hydrophobic seed particle, and the NaOH water solution of 1 % of the weight of concentration adjusted pH of dispersion liquid to 10. Then, the temperature up of these dispersion liquid was carried out to 80 degrees C, heating churning was performed for 60 minutes, subsequently it cooled to 30 degrees C, and 100g of ion exchange resin was added, alkali was removed enough, agitating dispersion liquid, the silica particle was separated and washed, and the seed particle (C3) subsequently dried and activated at 110 degrees C was obtained.

[0084] After adding the mixed solution (hexamethyldisilazane 25g and methyl alcohol 25g) to this and agitating to it for 12 hours, having made methyl alcohol 333g distribute 50g (C3) of activated seed particles, having irradiated the supersonic wave, having carried out mono dispersion of the seed particle

(C3), and agitating dispersion liquid, it dissociated, alcohol washed, subsequently it dried at 80 degrees C for 2 hours, and the hydrophobic seed particle (S-3) was obtained.

[0085] 526g of n-butanol water solutions of 5 % of the weight of concentration was made to distribute 10g (S-3) of growth hydrophobic seed particles of a seed particle, 1.2g of octyl sodium naphthalenesulfonate was added to these dispersion liquid as a surface active agent, and the supersonic wave was irradiated. Subsequently, methyl trimetoxysilane 60g was added and the dispersion liquid whose lower layer is a dispersion-liquid layer of a hydrophobic seed particle (S-3), whose upper layer is a layer of methyl trimetoxysilane and which were divided into two-layer were prepared. Subsequently, while the upper layer and a lower layer agitated 12.0g of NH₃ water solutions of 0.28 % of the weight of concentration in the dispersion-liquid layer of a hydrophobic seed particle (S-3) at extent which is not mixed completely, it added over 2 hours. Methyl trimetoxysilane was hydrolyzed performing churning further for about 2 hours until the upper layer of the methyl trimetoxysilane after addition of NH₃ water solution was lost, and polyorganosiloxane particle dispersion liquid (PS-3) were prepared.

[0086] After heat-treatment reaction termination of a polyorganosiloxane particle, after removing the very small gel generated by the reaction, it put at 80 degrees C for 12 hours. After having taken out the obtained particle, washing in ethanol and drying at 80 degrees C subsequently for 2 hours, it heat-treated in 3-hour air at 300 degrees C, and the polyorganosiloxane particle (P-3) was obtained. It asked for particle size distribution, a particle-size coefficient-of-variation CV value, and 10% compressibility about the obtained polyorganosiloxane particle.

[0087] A result is shown in Table 1. Moreover, as for the added methyl trimetoxysilane, 94.5% was used for particle growth. In addition, this activity ratio ** weight which subtracted the weight of a particle to the actually obtained seed particle by the weight computed noting that R₁nSi(OR₂)_{4-n} becomes polyorganosiloxane (R₁nSiO (4-n)/2) by hydrolysis, as shown in a bottom type.

[0088]

[Equation 3]

$$\text{収率} = \frac{(\text{実際に得られた粒子の重量}) - (\text{シード粒子の重量})}{\text{有機ケイ素化合物から計算されるポリシロキサン理論重量}} \times 100$$

* 実際に得られた粒子を 440℃で3時間加熱処理した重量 (g)

[0089]

[Example 4] Except having used the plastics particle (bridge formation system polymer of styrene) whose mean particle diameter is 5.5 micrometers as a growth seed particle of a seed particle, after performing hydrophobing processing like an example 3, the hydrophobic seed particle was grown up, and polyorganosiloxane particle dispersion liquid (PS-4) were prepared.

[0090] After heat-treatment reaction termination of a polyorganosiloxane particle, after removing minute gel, it put at 80 degrees C for 12 hours. After having taken out the obtained particle, washing in ethanol and drying at 80 degrees C subsequently for 2 hours, it heat-treated in 3-hour air at 300 degrees C, and the polyorganosiloxane particle (P-4) was obtained. It asked for particle size distribution, a particle-size coefficient-of-variation CV value, and 10% compressibility about the obtained polyorganosiloxane particle.

[0091] A result is shown in Table 1. In addition, as for the added methyl trimetoxysilane, 94.0% was used for particle growth.

[0092]

[Example 5] Methyl trimetoxysilane 750g was added calmly, having put in 6,581g of pure water and agitating in the container of preparation content volume 10L of a hydrophobic seed particle, and methyl trimetoxysilane and pure water considered as the condition of having separated into vertical two-layer one. Subsequently, it cooled, agitating the upper methyl trimetoxysilane. Separately, 1.35g of aqueous ammonia of butyl alcohol 3.49g and 28 % of the weight of concentration was added to 139.6g of pure water, and 7.5g (octyl naphthalene sulfonic-acid sodium) of anionic surface active agents was added to this. It added over 60 minutes, agitating to extent with which the upper layer and a lower layer do not mix this surfactant mixed solution completely in the lower layer (water layer) divided into vertical two-

layer one, churning was performed succeedingly for 2 hours, and the dispersion liquid of a hydrophobic seed particle (S-5) were prepared. The dispersion liquid of this seed particle (S-5) extracted the part, the seed particle was separated, washing desiccation was carried out, subsequently it calcinated at 300 degrees C for 2 hours, and seed particle powder was obtained. Mean particle diameter and particle diameter coefficient of variation (CV value) were measured about the obtained seed particle.

[0093] A result is shown in Table 1.

growth of a seed particle -- it added having applied methyl trimetoxysilane 600.8g, 2,352.8 g pure-water and butyl alcohol 58.9g, and the mixed liquor of 0.48g of aqueous ammonia of 28 % of the weight of concentration to the 1,496.6 g dispersion liquid of the occasion and the above-mentioned seed particle (S-5) for 6 hours, respectively, and polyorganosiloxane particle dispersion liquid (PS-5) were prepared.

[0094] The polyorganosiloxane particle was separated and washed from **** heat-treatment at this rate [of a polyorganosiloxane particle], and, subsequently it dried at 110 degrees C for 2 hours, subsequently it heat-treated at 300 degrees C for 3 hours, and the polyorganosiloxane particle (P-5) was obtained. Compressibility, mean particle diameter, and particle diameter coefficient of variation (CV value) were measured 10% about the obtained polyorganosiloxane particle.

[0095] A result is shown in Table 1. In addition, as for the added methyl trimetoxysilane, 94.8% was used for particle growth.

[0096]

[The example 1 of a comparison] The dispersion liquid of a seed particle were prepared like the example 1 except having not used the preparation surfactant of a seed particle. The part was extracted from seed particle dispersion liquid, the seed particle was separated and washed, subsequently it dried at 110 degrees C for 2 hours, the powder of a seed particle was obtained, and particle size distribution and a particle-size coefficient-of-variation CV value were calculated.

[0097] Consequently, mean particle diameter was 5.0 micrometers, a CV value is 10.4% and the big and rough particle and the very fine particle were accepted in part into the particle.

a seed particle -- ***** -- having had -- using 14,965.5 g seed particle dispersion liquid, particle growth was performed like the example 1 and polyorganosiloxane particle dispersion liquid were prepared.

[0098] The polyorganosiloxane particle was separated and washed from dispersion liquid, subsequently it dried at 110 degrees C for 2 hours, and the powder of a polyorganosiloxane small particle was obtained.

about the heat-treatment profit **** polyorganosiloxane particle of a polyorganosiloxane particle, under the nitrogen-gas-atmosphere mind containing 10% of ammonia gas, the heating place was carried out at 440 degrees C for 3 hours, and the polyorganosiloxane particle (P-6) was obtained.

[0099] About the obtained particle, particle size distribution, a particle-size coefficient-of-variation CV value, and 10% compressibility were measured similarly. A result is shown in Table 1. In addition, the yield of the particle calculated from the amount of theoretical generation of the particle calculated from the amount of the methyl trimetoxysilane used and the weight of the actually obtained particle was 45.0%.

[0100]

[Table 1]

表1

	疎水性シード粒子		ポリオルガノシロキサン微粒子		
	平均粒子径 μm	CV値 %	平均粒子径 μm	CV値 %	10%圧縮弾性率 kgf/mm^2
実施例1	5.2	2.4	13.1	1.9	450
実施例2	5.2	2.4	12.4	1.9	4780
実施例3	5.0	1.0	7.2	2.0	980
実施例4	5.5	2.8	6.8	2.2	420
実施例5	5.4	2.4	6.9	2.0	320
比較例1	5.0	10.4	7.8	12.1	425

[0101]

[Example 6] The substrate with a transparent electrode of a pair used for the liquid crystal cell of a liquid crystal display liquid crystal display was prepared. The orientation film with which the ITO thin film as a transparent electrode makes the orientation of the liquid crystallinity compound molecule which is formed and is further contained in the liquid crystal ingredient on this ITO thin film front face, as for this transparency substrate with a transparent electrode, carry out in the predetermined direction to one side of a glass substrate was formed.

[0102] Next, in the mixed solvent (350 cc [of pure water], and isopropyl alcohol 120cc, and ethyl alcohol 30cc), agitating the polyorganosiloxane particle (P-1) obtained in the example 1 so that concentration might become 1 % of the weight, irradiate a supersonic wave, it was made to distribute and the spray was prepared. Using the spraying nozzle (RUMINA--10) of 0.5mm of diameters phi of a nozzle, distance of a nozzle and an orientation film surface was set to 70cm, and this spray was sprayed on the orientation film surface of a transparency substrate front face with a transparent electrode by pressure 3 kg/cm², and it was sprinkled to the orientation film surface formed in one transparency substrate with a transparent electrode so that about 130 average particle spraying consistencies /might be set to 2 mm.

[0103] On the sprinkled polyorganosiloxane particle, the orientation film surface by which the form was carried out to the transparency substrate with a transparent electrode of another side was contacted, and the transparency substrate with both transparent electrodes was piled up. In this way, the clearance formed between the orientation film of a transparency substrate with both transparent electrodes was filled up with the liquid crystal ingredient, and the liquid crystal cell was produced lamination and by sealing by the resin for seals which contains the polyorganosiloxane particle (P-2) which manufactured the periphery section of both substrates in the example 2 2.5% of the weight. In addition, the liquid crystal cell produced in this way is driven in STN mode.

[0104] Although the actuation cooled from a room temperature at -40 degrees C to the produced liquid crystal cell was repeated 10 times and air bubbles were observed at -40 degrees C each time, low-temperature air bubbles were observed for neither inside the liquid crystal cell. Moreover, when the produced liquid crystal cell was attached in the liquid crystal display and the liquid crystal display was made to drive, the display nonuniformity of an image was not observed.

[0105] A result is shown in Table 2.

[0106]

[Examples 7-9] In the liquid crystal display example 6, although the liquid crystal display cel was created like the example 6 except having sprinkled and used - (P-5) for the polyorganosiloxane particle (P-3) and orientation film surface respectively instead of the polyorganosiloxane particle (P-1) and air bubbles were observed, low-temperature air bubbles were observed for neither inside the liquid crystal cell.

[0107] Moreover, when the liquid crystal cell created similarly was attached in the liquid crystal display and the liquid crystal display was made to drive, the display nonuniformity of an image was not observed. A result is shown in Table 2.

[0108]

[The example 2 of a comparison] Except having sprinkled and used for the orientation film surface the polyorganosiloxane particle (P-6) manufactured in the example 1 of a liquid crystal display comparison, when the liquid crystal display cel was created like the example 6 and air bubbles were observed, low-temperature air bubbles were observed inside the liquid crystal cell each time.

[0109] Moreover, when the liquid crystal cell created similarly was attached in the liquid crystal display and the liquid crystal display was made to drive, the display nonuniformity of an image was observed. A result is shown in Table 2.

[0110]

[Table 2]

表2

	ポリオルガノシロキサン微粒子		液晶表示装置	
	面内スペーサ	シール部スペーサ	低温気泡の発生	画像の表示ムラ
実施例6	P-1	P-2	なし	なし
実施例7	P-3	P-2	なし	なし
実施例8	P-4	P-2	なし	なし
実施例9	P-5	P-2	なし	なし
比較例1	P-6	P-2	あり	あり

[Translation done.]